Stability of small Ni–Ti bimetallic clusters studied by density functional theory*

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The low-energy structures and the electronic and the magnetic properties of small Ni_nTi_n ($n = 1$–6) and Ni_mTi_n ($1 \le n \le 4$, $1 \le m \le 4$, $n \ne m$) clusters are investigated by performing all-electron calculations based on density functional theory. Ground states and several isomers near the ground states are determined for these clusters. The results indicate that the growth of small Ni_mTi_n clusters prefers to form rich Ti–Ni and Ti–Ti bonds. When the percentage of titanium atoms is significantly greater than that of nickel atoms, the nickel atoms are most frequently found above the surface; in contrast, the titanium atoms prefer the bridging sites. A Mülliken spin population analysis indicates that the total spin of titanium-nickel clusters is not always zero.

Keywords: Ni_mTi_n clusters, lowest-energy structure, electronic and magnetic properties

PACC: 3120A, 3640B, 2110K

1. Introduction

Intensive study on homogeneous transition-metal (TM) clusters[1] has been conducted over the past two decades. Although some issues regarding pure TM clusters are still unclear to some extent, their geometrical structures, electronic properties, and magnetism are comprehensively understood. Beyond the pure metal clusters, however, nanoscale alloys[2−7] may offer the opportunity to tailor the properties of clusters through the choice of atomic types and compositions. In addition, they present a number of structures, phases and properties that are intrinsically different from those of corresponding pure metals. Titanium (Ti) and nickel (Ni) are respectively early TMs and late 3d TM atoms, whose electron configurations ($3d^24s^2$ and $3d^84s^2$ respectively) complement each other. Consequently, the interaction between these two kinds of atoms has attracted much attention in scientific and technological fields. For instance, the equiatomic NiTi alloys[8] are very interesting because of their remarkable shape memory effect, pseudoelasticity, and other excellent properties. Besides bulk NiTi materials, NiTi chains with linear and zigzag structures and NiTi particles[9,10] as small as 2–3 nm were studied recently both in experiment and in theory. A first-principles study showed that the stability of one-dimensional chains can be enhanced by alloying.[8] Molecular dynamics simulations and experimental observations[9] of nanoclusters synthesized by the bioreduction method suggested that Ni–Ti nanoclusters were not energetically favourable to the commonly considered geometrical arrangements. It is found that the Ni and Ti atoms tend to aggregate separately rather than form clusters containing both species. Much less attention[11] has been paid to the small mixed NiTi clusters. Venkataramanan[12] employed a density functional method with pseudopotential basis set CEP-121G to study the Ni_xTi_y ($x + y \le 5$) clusters and showed that the bimetallic clusters had shorter bond lengths and higher band gaps. Segregation was found to occur in the bimetallic systems and to have a certain geometry. It would therefore be interesting to elucidate the growth behaviour of small Ni–Ti bimetallic clusters and the size-dependent evolution of physical properties of the clusters. This may be also conducive to the understanding of the physical nature of higher-dimensional NiTi materials.

In cluster physics, one of the most fundamental problems is to determine the ground-state geometry of a cluster, since it may affect physicochemical be-

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haviour and various properties. Therefore, it is highly desirable to acquire accurate information about the structures of the smaller Ni–Ti species, which can give us more insight into the growth mechanisms and the properties of Ni–Ti alloys. In this work, a considerable number of possible initial structural isomers are designed for each cluster size, and all-electron calculations based on density functional theory (DFT) are carried out to obtain the total energy for each structure.

2. Computational details

In searching for the lowest-energy structures of the Ni_mTi_n clusters, the initial structures not only took those of pure TM clusters based on our previous studies[13−15] but also included some other reasonable geometries as appropriate ones. The number of structural candidates increases very rapidly, depending on the size of the cluster and its components. For example, ten initial configurations including one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) candidates were considered for Ni_2Ti_2, while the number of structural isomers increased to twenty for Ni_6Ti_6. The geometry optimizations were performed by using the spin-polarized DFT implemented in the Dmol^3 package.[16,17] The package is for an accurate and efficient density functional calculation where a rapidly convergent 3D numerical integration scheme for molecules is used. It has been fruitfully employed to study the ground state of highly correlated nanoscale materials, including clusters composed of Ni or Ti atoms.[13−15,18−20]

In the electronic structure calculations, an all-electron treatment with a double-numerical basis plus polarized functions (DNPs)[16] was chosen. Experimental evidence of the high reactivity of TM clusters suggests that their ground states have open shells, which means that in the density functional approach, spin polarized calculations are required to find a correct electronic configuration of the ground state. The exchange–correlation interaction was treated within the generalized gradient approximation (GGA) in which the Becke exchange functional[21] and the Lee–Yang–Parr correlation functional (BLYP)[22] were used. The accuracy of the present all-electron BLYP computational scheme was validated by benchmark calculations of Ni_n (n=2–13)[13] clusters and the Ti_n (n=2–13, 16, 43, 55) clusters.[19,20] Self-consistent-field calculations of total energy were carried out with a convergence criterion of 1×10^{-5} Hartree. In the geometry optimization, the convergence thresholds were set to be 2×10^{-3} Hartree/Bohr for the force, 5×10^{-3} Å (1 Å=0.1 nm) for the displacement, and 1×10^{-6} e/Å^3 for the charge density.

The binding energy of a cluster is defined as the difference in total energy between the interacting atom system and the free-atom system. Our calculations show that the bond lengths of Ti–Ti and Ni–Ni for Ti_2 and Ni_2 dimers are 1.974 Å and 2.112 Å, which are in good agreement with the experimental results 1.9429±0.0013 Å[23] and 2.1545±0.0005 Å,[24] respectively. The total spin (S) of the Ni_2 dimer is 1, which is consistent with the earlier matrix isolation measurements[25] and the theoretical prediction.[18] The triplet ground state of Ti_2 accords with Bauschlicher's result[26] obtained with the multi-reference configuration interaction method. The on-site charges and magnetic moment are evaluated via Mülliken population analysis.

3. Results and discussion

3.1. Ni_nTi_n (n = 1–6)

The optimized structures of the Ni_nTi_n (n=2–6) clusters are shown in Fig. 1. The calculated results for various configurations are listed in Table 1.

For the NiTi dimer, a triplet state is found to be the ground state. The computed bond length is 2.087 Å, which is in good agreement with the previous theoretical result.[11] The vibrational frequency is 356.7 cm^{-1}, which is quite consistent with both the experimental value[27] and the previous theoretical result.[11] The local spin magnetic moments of Ni atom and Ti atom are –0.141 μ_B and 2.141 μ_B, respectively. From the spin density of the NiTi dimer in Fig. 2, we can see that the 3d electrons of the titanium atom make the main contribution to the spin of the cluster. There is a charge transfer of 0.2e from Ti atom to Ni atom, where e represents the electron charge. This is in agreement with the conclusions of the bonding model[28] for an early-late transition bulk metal.

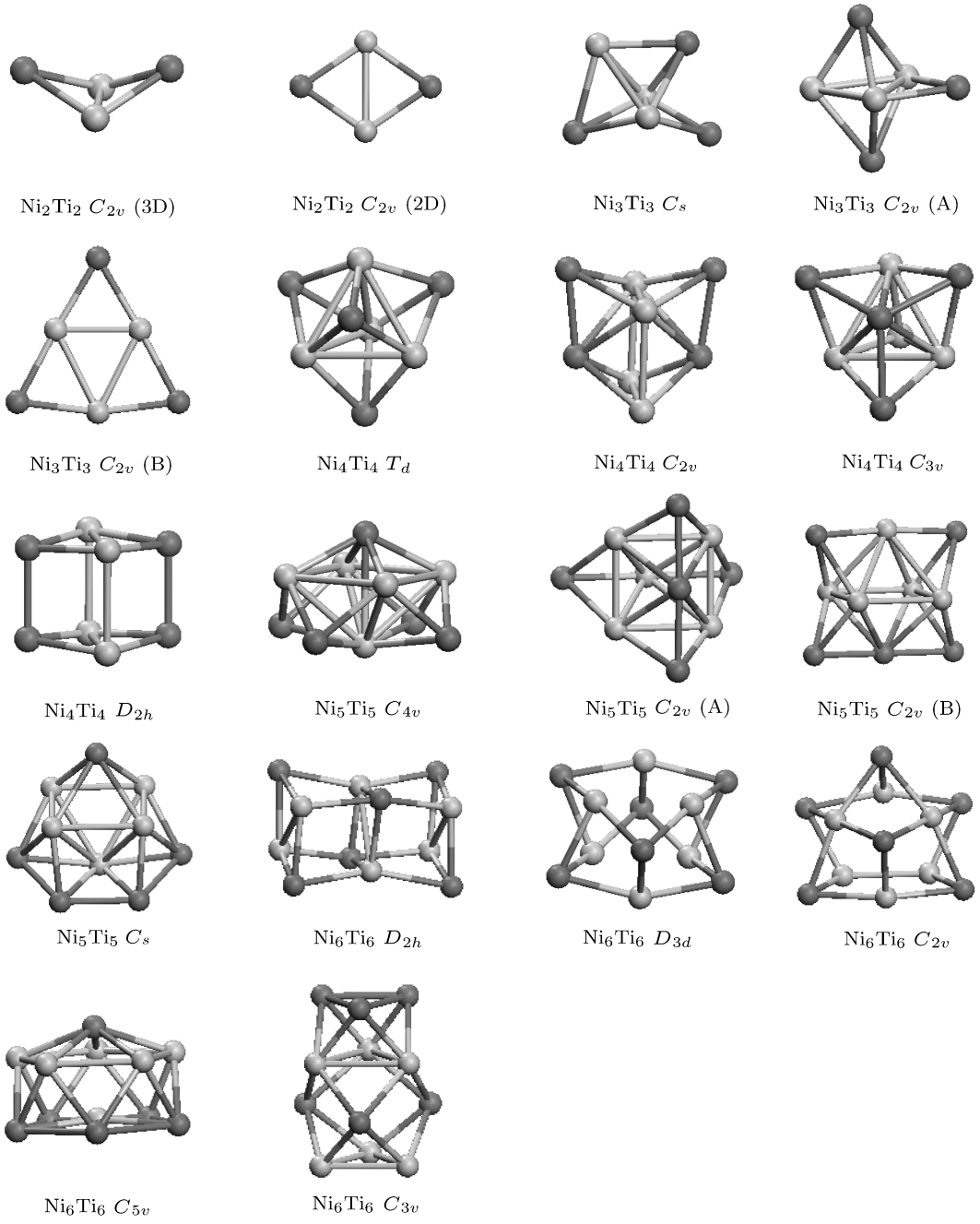


Fig. 1. Structures and their symmetries for the low-lying isomers of Ni_nTi_n (n=2–6) clusters. Dark spheres represent Ni atoms, and light spheres represent Ti atoms.

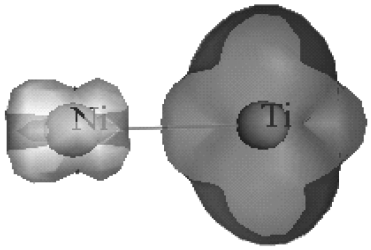


Fig. 2. Spin density of the NiTi dimer, where the isovalue is set at 0.04.

In the case of Ni_2Ti_2, two stable C_{2v} structures are found. From Fig. 1, we can see that the four atoms in Ni_2Ti_2 are bonded through Ti–Ti and Ni–Ti bonds but no Ni–Ni bonds occur. The rhombus C_{2v} (2D) is only 0.06994 eV higher in energy than the ground state C_{2v} (3D). For Ni_3Ti_3, the structure with C_s symmetry is stablest. The C_{2v} (3D) and C_{2v} (2D) structures are both low-lying states with very close-lying energies. None of them has Ni–Ni bonds. The number of bonds

in the lowest-energy structure is largest in these three structures. For Ni_4Ti_4, four geometric isomers, T_d, C_{2v}, C_{3v}, D_{2h}, have been found. The interior framework of the lowest-energy T_d structure is composed of titanium atoms with no Ni–Ni bonds. For Ni_5Ti_5, we have found four low-lying isomers, C_{4v}, C_{2v} (A), C_{2v}(B) and C_s, whose interior frameworks are all composed of titanium atoms. Only the third isomer C_{2v} (B) and the fourth isomer C_s have a few Ni–Ni bonds. For Ni_6Ti_6, we have found five low-lying states with very close-lying energies. The ground state D_{2h} is entirely composed of Ni–Ti and Ti–Ti bonds. From the above, it is clear that in Ni_nTi_n clusters the bonding between Ti and Ti forms a main interior framework and there exist rich Ni–Ti bonds but few Ni–Ni bonds.

Table 1. Calculated results for different structures of Ni_nTi_n (n=1–6) clusters, i.e. symmetry, binding energy E_b (in eV), highest occupied molecular orbital (HOMO) state, energy difference ΔE between lowest occupied molecular orbital (LUMO) and HOMO, total spin moment μ_s (in μ_B), and electron occupation number n in HOMO.

	sym	HOMO	E_b	ΔE	μ_s	n
NiTi	C_{*v}	A1	–5.29935	0.739	2	1
Ni_2Ti_2	C_{2v} (3D)	B2	–13.14275	0.233	2	1
	C_{2v} (2D)	B3U	–13.07281	0.485	4	1
Ni_3Ti_3	C_s	A′	–22.48626	0.583	0	1
	C_{2v} (A)	A1	–22.43900	0.574	0	1
	C_{2v} (B)	A1	–21.72905	0.106	0	1
Ni_4Ti_4	T_d	T2	–32.54026	0.440	0	3
	C_{2v}	B1	–31.08756	0.133	2	1
	C_{3v}	E	–30.94804	0.166	2	2
	D_{2h}	B3G	–30.13780	0.203	4	1
Ni_5Ti_5	C_{4v}	A1	–40.72262	0.207	4	1
	C_{2v} (A)	A1	–40.33626	0.249	2	1
	C_{2v} (B)	A1	-40.28540	0.272	2	1
	C_s	A″	–40.18302	0.181	0	1
Ni_6Ti_6	D_{2h}	B1U	–50.44855	0.169	2	1
	D_{3d}	A2U	–50.24771	0.264	0	1
	C_{2v}	A2	–49.99059	0.082	2	1
	C_{5v}	A1	–49.47960	0.315	0	1
	C_{3v}	E	–49.26217	0.332	0	2

3.2. Ni_nTi (n = 2–4)

The lowest-energy structures and some interesting low-lying metastable isomers for Ni_nTi (n=2–4) are shown in Fig. 3. The calculated results for various configurations are listed in Table 2.

Table 2. Calculated results for different structures of Ni_nTi (n=2–4) clusters, i.e. symmetry, binding energy E_b (in eV), HOMO state, energy difference ΔE between LUMO and HOMO, total spin moment μ_s (in μ_B), and electron occupation number n in HOMO.

	sym	HOMO	E_b	ΔE	μ_s	n
Ni_2Ti	C_{2v}	B1	–9.53778	0.665	0	1
	D_{*h}	A1	–9.29645	0.236	0	1
Ni_3Ti	C_{2v} (A)	A2	-13.98276	0.971	0	1
	C_{2v} (B)	A1	–13.64512	0.774	0	1
	C_{3v}	A2	–13.36483	0.482	2	1
	C_{2v} (C)	A1	–12.83038	0.257	0	1
Ni_4Ti	C_{2v} (A)	B1	–18.20699	0.413	0	1
	C_{4v}	E2	–18.19987	0.225	2	2
	C_{2v} (B)	B1	–18.01906	0.382	2	1
	D_{2h}	B2U	–17.64585	0.559	0	1
	C_{3v}	A1	–17.52559	0.465	0	1

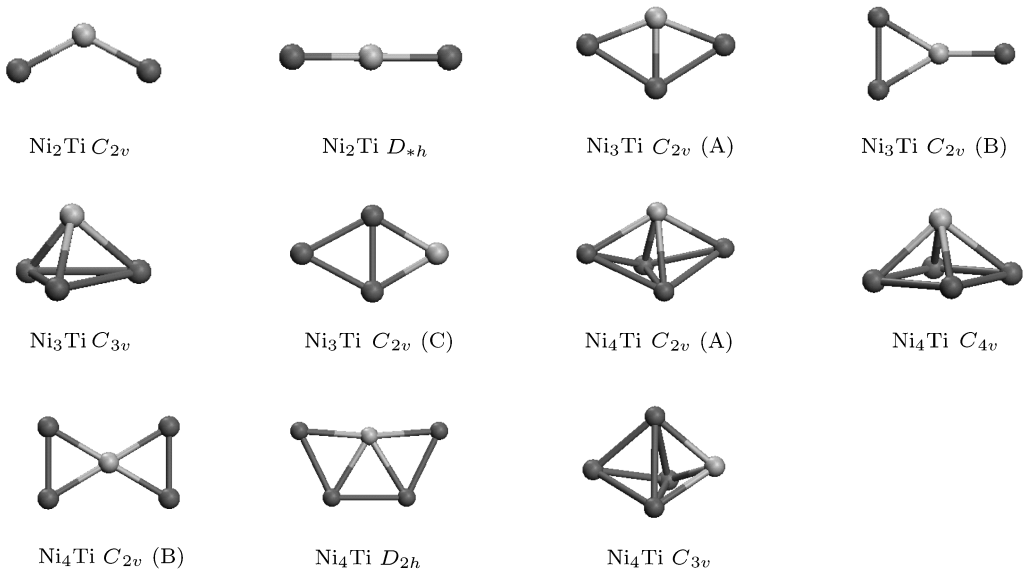


Fig. 3. Structures and their symmetries for the low-lying isomers of Ni_nTi (n=2–4) clusters, where dark spheres represent Ni atoms and light spheres denote Ti atoms.

The ground state of the Ni_2Ti cluster is a bent structure with two Ti–Ni bonds. The calculated bond length and the bond angle between the two Ti–Ni bonds are 2.074 Å and 123°, respectively. For linear structures, we find that the D_{*h} configuration with a Ti atom in the middle is stablest, being 0.24133 eV higher in energy than the bent structure. In the case of Ni_4, the ground-state structure adopts a distorted tetrahedron structure with D_{2d} symmetry.[15] However, the four-atom cluster Ni_3Ti has a C_{2v} (A) rhombus structure. The triangular pyramid with C_{3v} symmetry is 0.61793 eV and 0.28029 eV higher in energy than the planar rhombus C_{2v} (A) and Y-type C_{2v} (B), respectively. For Ni_4Ti, there exist five low-lying isomers with C_{2v} (A), C_{4v}, C_{2v} (B), D_{2h}, and C_{3v} symmetries, respectively. The three-dimensional C_{2v} (A) configuration has a lowest-energy structure. The C_{2v} (A) and the C_{3v} isomers have the same triangular bipyramid frameworks, but the positions of Ti atoms are different. In the C_{2v} (A) structure the Ti atom occupies the bridging site. In the C_{3v} structure the Ti atom occupies the vertex site of the triangle surface. The latter's energy is 0.6814 eV higher than the former's. The above analyses indicate that the doping Ti atom prefers to occupy the bridge site in Ni_nTi (n=2–4) clusters.

3.3. $NiTi_n$ (n = 2–4)

The geometrical structures of low-lying isomers for $NiTi_n$ (n=2–4) clusters are shown in Fig. 4. The calculated results for various configurations are listed in Table 3.

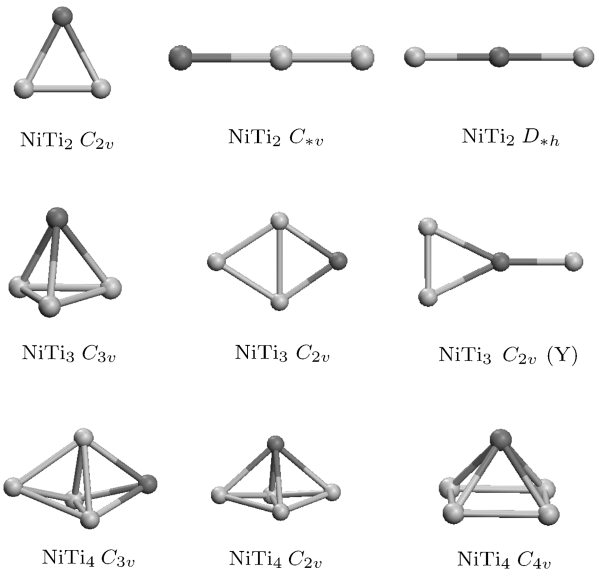


Fig. 4. Structures and their symmetries for the low-lying isomers of $NiTi_n$ (n=2–4) clusters, where dark spheres represent Ni atoms and light spheres denote Ti atoms.

For the $NiTi_2$ cluster, we have carried out calculations for three structures: the C_{2v} planar form and the two linear chains C_{*v} and D_{*h}. The lowest-

energy structure is an isosceles triangle with two Ti–Ni bonds of length 2.349 Å and one Ti–Ti bond of length 2.184 Å. The second-lowest energy isomer is the linear chain C_{*v} with the Ti atom in the middle. For $NiTi_3$, we have studied three configurations: the tetrahedron C_{3v}, the planar rhombus C_{2v} and the Y-type C_{2v} (Y). The lowest-energy structure obtained is the C_{3v} structure with three Ti–Ti and three Ti–Ni bonds. Here, the Ni atom occupies the vertex site of the triangular surface. From Fig. 4, we can see that the number of bonds in the C_{3v} configuration is largest in the three low-lying isomers. For $NiTi_4$, we have found three low-lying isomers which have C_{3v}, C_{2v} and C_{4v} symmetry, respectively. The lowest-energy structure is the trigonal bipyramid (C_{3v} symmetry) structure in which the Ni atom also occupies the vertex site of the triangle surface. The second-lowest C_{2v} structure has the same framework as the C_{3v} ground state, in which the Ni atom occupies the bridge site. The above analyses indicate that the doping Ni atom prefers the vertex site of the surface in $NiTi_n$ (n=2–4) clusters.

Table 3. Calculated results for different structures of $NiTi_n$ (n=2–4) clusters, i.e. symmetry, binding energy E_b (in eV), HOMO state, energy difference ΔE between LUMO and HOMO, total spin moment μ_s (in μ_B), and electron occupation number n in the HOMO.

	sym	HOMO	E_b	ΔE	μ_s	n
$NiTi_2$	C_{2v}	B2	–8.02626	0.217	2	1
	C_{*v}	B1	–7.54591	0.414	0	1
	D_{*h}	A2U	–7.25528	0.440	4	1
$NiTi_3$	C_{3v}	A1	–11.84357	0.656	0	1
	C_{2v}	A1	–11.69825	0.422	2	1
	C_{2v} (Y)	B2	–10.52203	0.677	4	1
$NiTi_4$	C_{3v}	A1	–15.80798	0.348	6	1
	C_{2v}	B2	–15.40501	0.270	2	1
	C_{4v}	B1	–14.78795	0.269	4	1

3.4. Ni_mTi_n (m, n=2–4, $m \neq n$)

The geometrical structures of some low-lying isomers of Ni_mTi_n (m, n=2–4, $m \neq n$) clusters are shown in Fig. 5. The calculated results for various isomers are listed in Table 4.

For Ni_3Ti_2 and Ni_2Ti_3, the D_{3h} symmetry is found to provide the stablest structure with a single HOMO state. The minority Ti atoms of the Ni_3Ti_2 cluster tend to occupy the bridge sites. However, the minority of Ni atoms of the Ni_2Ti_3 cluster occupy the vertex sites of the triangle surface, especially in the lowest-energy D_{3h} structure. The binding energies of the planar structures are obviously higher than those of the 3D growth modes. The four lowest-energy isomers have been determined for Ni_4Ti_2. The Ti atoms occupy the vertex site of the base surface in the D_{4h} structure. For Ni_2Ti_4, we have investigated three configurations. The bi-capped tetrahedron C_{2v} structure is stablest; the HOMO state is a singlet. The rectangular bipyramid D_{4h} structure has a twofold HOMO state and is unstable according to Jahn–Teller theory.[29] We have found a stabler C_{2h} structure based on the structural distortion of the D_{4h} structure. For each of Ni_4Ti_3 and Ni_3Ti_4, we have found eight low-lying isomers. Structural analysis of these two clusters with near equiatomic composition indicates a delamination growth of the two kinds of atoms.

Table 4. Calculated results for different structures of Ni_mTi_n (m, n=2–4, $m \neq n$) clusters, i.e. symmetry, binding energy E_b (in eV), HOMO state, energy difference ΔE between LUMO and HOMO, total spin moment μ_s (in μ_B), and electron occupation number n in the HOMO.

	sym	HOMO	E_b	ΔE	μ_s	n
Ni_3Ti_2	D_{3h}	A2	–18.08128	0.529	0	1
	C_{2v} (A)	A1	–17.88090	0.248	0	1
	C_{2v} (B)	A1	–17.26336	0.018	2	1
	C_{2v} (C)	A1	–16.92784	0.018	2	1
	C_{2v} (D)	B1	–16.17131	0.328	2	1
Ni_2Ti_3	D_{3h}	A1	–17.39621	0.667	0	1
	C_s	A	–16.78713	0.284	2	1
	C_{2v}	A1	–16.21195	0.407	0	1
Ni_4Ti_2	D_{4h}	A2U	–23.24735	0.540	0	1
	C_{2v} (A)	B1	–22.65277	0.603	0	1
	C_{2v} (B)	A1	–22.54531	0.287	0	1
	C_{2v} (C)	A2	–21.69162	0.758	0	1
Ni_2Ti_4	C_{2v}	B1	–21.37713	0.492	0	1
	C_{2h}	AG	–20.74872	0.373	4	1
	D_{4h}	EG	–20.64075	0.189	6	2
Ni_4Ti_3	C_s (A)	A	–27.58256	0.543	0	1
	C_{2v} (A)	B1	–27.46707	0.580	0	1
	C_{3v} (A)	A1	–27.19366	0.308	0	1
	C_{3v} (B)	E2	–27.18791	0.461	4	2
	C_s (B)	A	–27.13697	0.276	0	1
	C_s (C)	A	–26.97579	0.159	2	1
	C_{3v} (C)	E.	–26.86087	0.233	2	2
	C_{2v}	A2	–26.82506	0.300	0	1
Ni_3Ti_4	C_{3v}(A)	A1	–26.91552	0.448	0	1
	C_{2v} (A)	B2	–26.16100	0.385	0	1
	C_s (A)	A	–25.78178	0.330	0	1
	C_s (B)	A	–25.34216	0.135	2	1
	C_{2v} (B)	A2	–25.03005	0.110	2	1
	C_{3v} (B)	E	–24.71291	0.340	2	1
	C_{2v} (C)	A1	–24.45742	0.238	6	1
	C_{2v} (D)	B2	–24.42447	0.151	6	1

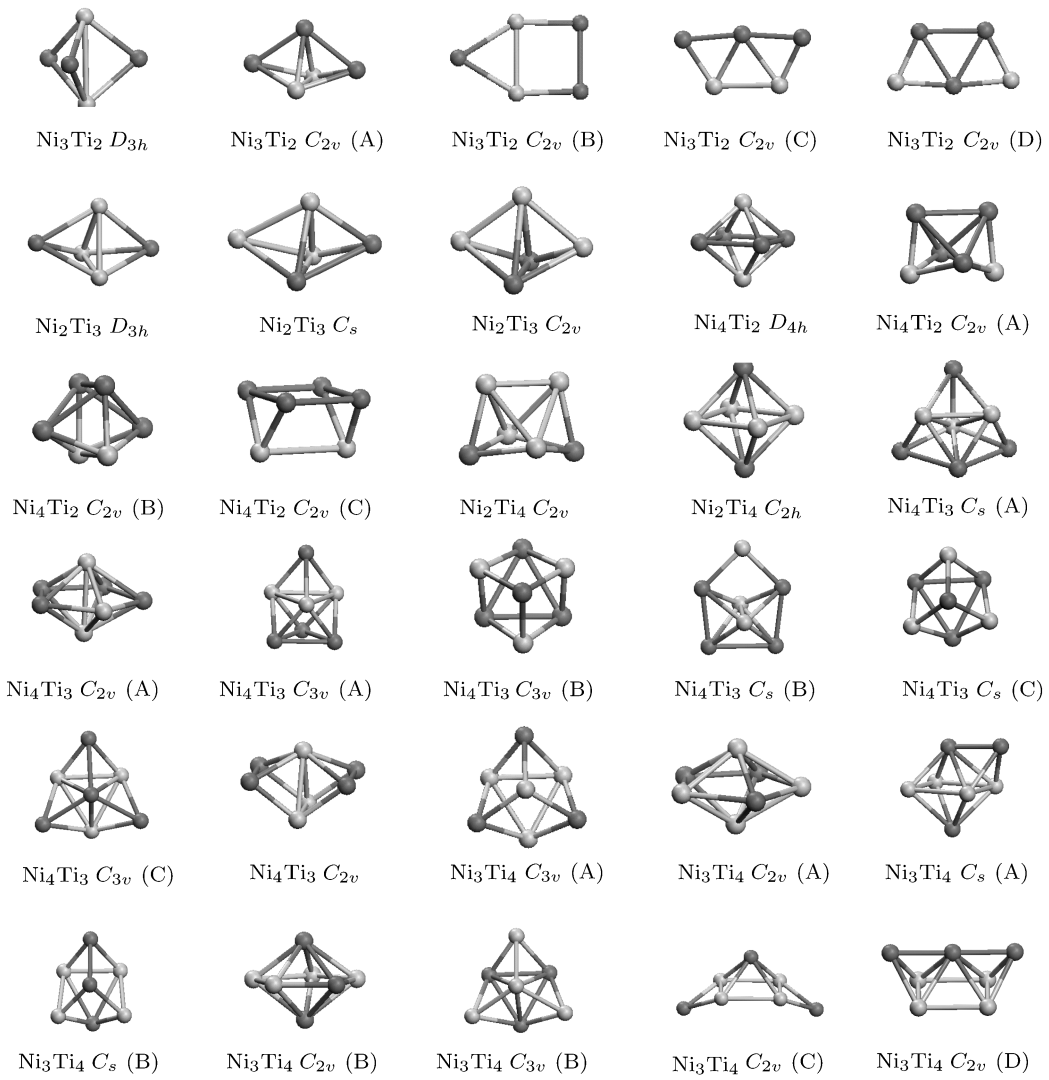


Fig. 5. Structures and their symmetries for the low-lying isomers of Ni_mTi_n (m, n=2–4, $m \neq n$) clusters, where dark spheres represent Ni atoms and light spheres denote Ti atoms.

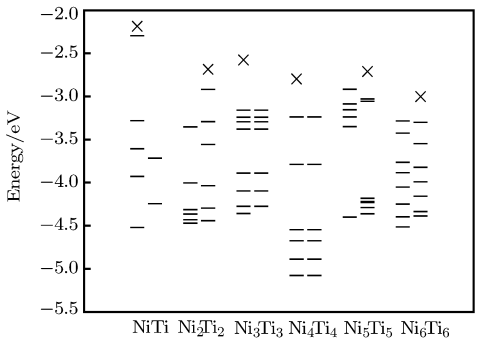


Fig. 6. Energy levels of the ground states for Ni_nTi_n (n=1–6) clusters. Solid lines refer to the occupied states, "×" refers to unoccupied states. For each cluster, two level diagrams are given. The one on the left of each pair denotes the spin-up states while that on the right denotes the spin-down states.

Although it is widely believed that NiTi alloys show no magnetism, the Mülliken spin population analysis indicates that the total spin of titanium–nickel clusters is not always zero. For $NiTi_n$ ($n \leq 4$) clusters with the exception of the $NiTi_3$ cluster, the clusters are all magnetic.

For Ni_nTi_n ($n \leq 6$) clusters, the Ni_5Ti_5 and Ni_6Ti_6 have obvious magnetic moments. Only in the case of the ground states of Ni_3Ti_3 and Ni_4Ti_4 clusters can the spin be zero. This is because they just form close-shell systems, and all electrons pair up with each other as clearly seen from Fig. 6

4. Summary

A number of low-lying isomers are explored and the lowest-energy structures for Ni_nTi_n (n=1–6) and Ni_mTi_n ($1 \leq n \leq 4$, $1 \leq m \leq 4$) clusters are determined by using first-principles calculations based on all-electron DFT. The results indicate that when the percentage of titanium atoms is significantly larger than that of nickel atoms, the nickel atoms are most frequently found above the surface; in contrast, the titanium atoms prefer the bridging sites. The growth of Ni_mTi_n clusters shows that the bonding between Ti and Ti is strong and forms an interior framework. There exist rich Ni–Ti bonds but only a few Ni–Ni bonds, which implies that the Ti–Ti bonds and the Ti–Ni bonds play an important role in reducing the energy. A Mülliken spin population analysis indicates that the charge generally tends to transfer from the titanium atoms to the nickel atoms and that the total spin of titanium–nickel clusters is not always zero.

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